

## 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

twin lattice in crossing the twin boundary was presented by Santoro (1974, equation 36). This measure is the difference between the metric tensors of lattice 1 and of lattice 2, the latter after retransformation by the existing or assumed twin operation (or more general orientation operation).

3.3.8.6. *Twinning of isostructural crystals*

In the present section, the critical discussion of the lattice theory of twinning is extended from the individual crystal species, treated in Section 3.3.8.5, to the occurrence of *merohedral twinning* in series of *isotypic* and *homeotypic* crystals. The crystals in each series have the same (or closely related) structure, space group, lattice type and lattice coincidences. The following cases are of interest here:

(i) Quartz ( $\text{SiO}_2$ ), quartz-homeotypic gallium phosphate ( $\text{GaPO}_4$ ) and benzil [ $(\text{C}_6\text{H}_5\text{CO})_2$ , so-called ‘organic quartz’] crystallize under normal conditions in the enantiomorphic space groups  $P3_121$  and  $P3_221$ . In quartz, merohedral Dauphiné and Brazil  $\Sigma 1$  twins are very frequent, whereas twins of the Leydolt (or ‘combined’) law are very rare (*cf.* Example 3.3.6.4). In gallium phosphate, Leydolt twins occur as frequently as Dauphiné and Brazil twins (Engel *et al.*, 1989). In benzil crystals, however, these twins are never observed, although the same space-group symmetries and conditions for systematic lattice coincidences as in quartz and in gallium phosphate exist. The reason is the completely different structure and chemical bonding of benzil, which is not capable of forming low-energy boundaries for these three twin laws.

(ii) Iron borate  $\text{FeBO}_3$ , calcite  $\text{CaCO}_3$  and sodium nitrate  $\text{NaNO}_3$  crystallize under normal conditions in the calcite structure with space group  $R32/c$ . The rhombohedral lattice allows twinning with a hexagonal  $\Sigma 3$  coincidence lattice (*cf.* Example 3.3.6.6). Practically all spontaneously nucleated  $\text{FeBO}_3$  crystals grown from vapour (chemical transport) or solution (flux) are  $\Sigma 3$ -twinned and form intergrowths of reverse and obverse rhombohedra (penetration twins). This kind of twinning is comparatively rare in calcite, where the twins usually appear with another morphology [contact twins on (0001)]. Interestingly, this  $\Sigma 3$  twinning does not occur (or is extremely rare) in sodium nitrate. This shows that even for isotypic crystals, the tendency to form  $\Sigma 3$  twins is extremely different. This can also be observed for crystals with the sodium chloride structure. Crystals of the silver halogenides  $\text{AgCl}$  and  $\text{AgBr}$ , precipitated from aqueous solution, develop multiple  $\Sigma 3$  twins with high frequency (Bögels *et al.*, 1999), and so does galena  $\text{PbS}$ , whereas the isotypic alkali halogenides (*e.g.*  $\text{NaCl}$ ,  $\text{LiF}$ ) practically never (or only extremely rarely) form  $\Sigma 3$  twins.

(iii) Another instructive example is provided by the  $\Sigma 3$  (111) spinel twins in the sphalerite ( $\text{ZnS}$ ) structure of III–V and II–VI semiconductor crystals (*cf.* Example 3.3.6.7). In some of these compounds this kind of twinning is quite rare (*e.g.* in  $\text{GaAs}$ ), but in others (*e.g.*  $\text{InP}$ ,  $\text{CdTe}$ ) it is very frequent. Gottschalk *et al.* (1978) have quantitatively shown that the ease and frequency of twin formation is governed by the (111) stacking-fault energy [which is the energy of the (111) twin boundary]. They have calculated the (111) stacking-fault energies of various III–V semiconductors, taking into account the different ionicities of the bonds. The results prove quantitatively that the frequency of the  $\Sigma 3$  twin formation is correlated with the (111) boundary energy.

These examples corroborate the early observations of Cahn (1954, pp. 387–388). The present authors agree with his elegantly formulated conclusion, ‘that the fact that two substances are isostructural is but a slender guide to a possible similarity in their twinning behaviour’.

3.3.8.7. *Conclusions*

In conclusion, the *lattice theory of twinning*, presented in this section, can be summarized as follows:

(i) The lattice theory represents one of the first systematic theories of twinning; it is based on a clear and well defined concept and thus has found widespread acceptance, especially for the description, characterization and classification of ‘triperiodic’ (merohedral and pseudo-merohedral) twins.

(ii) The concept, however, is purely *geometrical* and has as its object a mathematical, not a physical, item, the *lattice*. It takes into account neither the crystal structure nor the orientation and energy of the twin interface. This deficit has been pointed out and critically discussed as early as 1905 by Mügge, and later by Burgers (1927, 1932), Heide (1928), Buerger (1945), Cahn (1954, Section 1.3), Hartman (1956) and Holser (1958, 1960); it is the major reason for the limitations of the theory and its low power of prediction for actual cases of twinning.

(iii) The relations between twinning and lattice (pseudo-) symmetries, however, become immediately obvious and are proven by many observations as soon as *structural pseudosymmetries* exist. Twinning is always facilitated if a real or hypothetical ‘parent structure’ exists from which the twin law and the interface can be derived. Here, the *lattice pseudosymmetry* appears as a necessary consequence of the *structural pseudosymmetry*, which usually involves only small deformations of the parent structure, resulting in small obliquities of twin planes and twin axes (which are symmetry elements of the parent structure) and, hence, in twin interfaces of low energy. These structural pseudosymmetries are the result either of actual or hypothetical phase transitions (domain structures, *cf.* Chapter 3.4) or of structural relationships to a high-symmetry ‘prototype’ structure, as explained in Section 3.3.7.2.

The importance of structural pseudosymmetries was emphasized as early as 1927 by Burgers. His statement (‘the possibility of the twinning must, therefore, be connected with a definite pseudo-symmetrical character of the structure of the untwinned crystal’), however, was seriously attacked by Friedel (1928): *La formation de la macle est totalement indifférente à la symétrie ou à la pseudo-symétrie de l’édifice cristallin ou des groupes d’atomes qui le constituent. Elle est due uniquement à la rencontre des symétries ou de pseudo-symétries dans les périodes (mailles, simples ou multiples) de cet édifice* (‘The formation of a twin is totally independent of the symmetry or pseudosymmetry of the crystal structure or the groups of atoms which build it. It is uniquely due to the presence of symmetries or pseudosymmetries of the lattice [simple or multiple unit cells] of the crystal’). In a reply to this paper, Burgers (1932) corroborates his previous criticism by the statement ‘that the fundamental cause of twinning must be looked for in the force relations in the immediate neighbourhood of the last-formed layer of the growing crystal’. In his view the (pseudo)symmetry of the simple or multiple lattice of a twinned crystal ‘is only another manifestation of a pseudo-symmetrical character of the structure of the untwinned crystal as a whole’.

(iv) On the other hand, twinning quite often occurs without recognizable structural pseudosymmetry, *e.g.* the (100) dovetail twins and the (001) Montmartre twins of gypsum, as well as the (101) and (301) reflection twins of rutile and some further examples listed in Table 3.3.8.2. In all these cases, it can be concluded that the lattice theory of twinning is not the suitable tool for the characterization and prediction of the twins; in the terminology of Friedel: the twins are not ‘triperiodic’ but only ‘diperiodic’ or ‘monoperiodic’.

3.3.9. *Twinning by merohedry and pseudo-merohedry*

We now resume the discussion of Section 3.3.8 on three-dimensional coincidence lattices and pseudo-coincidence lattices and apply it to actual cases of twinning, *i.e.* we treat in the present section *twinning by merohedry* (‘*macles par mériédrie*’) and *twinning by pseudo-merohedry* (‘*macles par pseudo-mériédrie*’),

### 3.3. TWINNING OF CRYSTALS

both for lattice index  $[j] = 1$  and  $[j] > 1$ , as introduced by Friedel (1926, p. 434). Often (strict) merohedral twins are called ‘parallel-lattice twins’ or ‘twins with parallel axes’. Donnay & Donnay (1974) have introduced the terms *twinning by twin-lattice symmetry* (TLS) for merohedral twinning and *twinning by twin-lattice quasi-symmetry* (TLQS) for pseudo-merohedral twinning, but we shall use here the original terms introduced by Friedel.

#### 3.3.9.1. Definitions of merohedry

In the context of twinning, the term ‘merohedry’ is applied with two different meanings which should be clearly distinguished in order to avoid confusion. The two cases are:

##### Case (1): ‘Merohedry’ of point groups

A merohedral point group is a subgroup of the holohedral point group (lattice point group) of a given Bravais lattice in a crystal family, *i.e.* group and subgroup belong to the same Bravais system. This is the original sense of the term *merohedry*, which has the morphological meaning of reduction of the number of faces of a given crystal form as compared with a *holohedral* crystal form. The degree of merohedry is given by the subgroup index  $[i]$ . For point groups within the same crystal family, possible indices  $[i]$  are 2 (hemihedry), 4 (tetartohedry) and 8 (ogdohedry). The only example for  $[i] = 8$  is the point group 3 in the hexagonal holohedry  $6/m2/m2/m$ .

If the point group of a crystal is reduced to such an extent that the subgroup belongs to a crystal family of lower symmetry, this subgroup is called a *pseudo-merohedral* point group, provided that the structural differences and, hence, also the metrical changes of the lattice (axial ratios) are small. Twinning by merohedry corresponds to non-ferroelastic phase transitions, twinning by pseudo-merohedry to ferroelastic phase transitions.

Both merohedral and pseudo-merohedral subgroups of point groups are listed in Section 10.1.3 and Fig. 10.1.3.2 of Volume A of this series (Hahn & Klapper, 2005); *cf.* also Koch (2004), Table 1.3.4.1.

##### Case (2): ‘Merohedry’ of translation groups (lattices)

The term ‘reticular’ or ‘lattice merohedry’ designates the relation between a lattice and its ‘diluted’ sublattice (without consideration of their lattice point groups). A sublattice<sup>6</sup> is a three-dimensional subset of lattice points of a given lattice and corresponds to a subgroup of index  $[j] > 1$  of the original translation group. This kind of group–subgroup relation has been called ‘reticular merohedry’ (*‘mériédrie réticulaire’*) by Friedel (1926, p. 444). Note that the lattice and its sublattice may belong to different crystal systems, and that the lattice point groups (holohedries) of lattice and sublattice generally do not obey a group–subgroup relation. This is illustrated by a cubic  $P$  lattice (lattice point group  $4/m\bar{3}2/m$ ) and one of its monoclinic sublattices (lattice point group  $2/m$ ) defined by a general lattice plane ( $hkl$ ) and the lattice row  $[hkl]$  normal to it. The symmetry direction  $[hkl]$  of the monoclinic sublattice does not coincide with any of the symmetry directions of the cubic lattice, *i.e.* there is no group–subgroup relation of the lattice point groups. The subgroup common to both (the intersection group) is only  $\bar{1}$ . A somewhat more complicated example is the  $[j] = 5$  ( $\Sigma 5$ ) sublattice obtained by a (210) twin reflection of a tetragonal crystal lattice; *cf.* Fig. 3.3.8.1 and Section 3.3.11.4.2. Both lattice and sublattice are tetragonal,  $4/mmm$ , with common  $c$  axes, but the intersection group of their holohedries is only  $4/m$ , the further symmetry elements are oriented differently.

Friedel (1926, p. 449) also introduced the term ‘reticular pseudo-merohedry’ (*‘pseudo-mériédrie réticulaire’*). This notion, however, can not be applied to a single lattice and its sublattice (a

single lattice can be *truly* diluted but not *pseudo*-diluted), but requires pseudo-coincidence of two or more superimposed lattices, which form a ‘pseudo-sublattice’ of index  $[j] > 1$ , as described in Section 3.3.8.4.

Because of this complicating and confusing situation we avoid here the term *merohedry* in connection with lattices and translation groups. Instead, the terms *coincidence(-site) lattice*, *twin lattice* or *sublattice* of index  $[j]$  are preferred, as explained in Section 3.3.8.2(iv). Note that we also use two different symbols  $[i]$  and  $[j]$  to distinguish the subgroup indices of point groups and of lattices.

#### 3.3.9.2. Types of twins by merohedry and pseudo-merohedry

Both kinds of merohedries and pseudo-merohedries were used by Mallard (1879) and especially by Friedel (1904, 1926) and the French School in their treatment of twinning. Based on the concepts of exact coincidence (merohedry,  $[j] = 1$ ), approximate coincidence (pseudo-merohedry) and partial coincidence (twin lattice index  $[j] > 1$ ), four major categories of ‘triperiodic’ twins were distinguished by Friedel and are explained below.

##### 3.3.9.2.1. Merohedral twins of lattice index $[j] = 1$

Here the lattices of all twin partners are parallel and *coincide exactly*. Consequently, all twin operations are symmetry operations of the lattice point symmetry (holohedral point group), but not of the point group of the structure. Here the term ‘merohedry’ refers to point groups only, *i.e.* to Case (1) above. Experimentally, in single-crystal X-ray diffraction diagrams all reflections coincide exactly, and tensorial properties of second rank (*e.g.* birefringence, dielectricity, electrical conductivity) are not influenced by this kind of twinning.

Typical examples of merohedral twins are:

(1) *Quartz*: Dauphiné, Brazil and Leydolt twins (*cf.* Example 3.3.6.4).

(2) *Pyrite*, iron-cross twins: crystals of cubic *eigensymmetry*  $2/m\bar{3}$  form penetration twins of peculiar morphology by reflection on (110), with  $[i] = 2$ .

(3) *KLiSO<sub>4</sub>*: the room-temperature phase III of *eigensymmetry* 6 exhibits four domain states related by three merohedral twin laws. These growth twins of index  $[i] = 4$  have been characterized in detail by optical activity, pyroelectricity and X-ray topography (Klapper *et al.*, 1987).

(4) *Potassium titanyl phosphate, KTiOPO<sub>4</sub>*: polar point group  $mm2$ , forms inversion twins (ferroelectric domains) below its Curie temperature of 1209 K.

##### 3.3.9.2.2. Pseudo-merohedral twins of lattice index $[j] = 1$

These twins are characterized by pseudo-merohedry of point groups, Case (1) in Section 3.3.9.1. The following examples are based on *structural pseudosymmetry* and consequently also on lattice pseudosymmetry, either as the result of phase transformations or of structural relationships:

(1) Transformation twins of *Rochelle salt* (Jona & Shirane, 1962): this ferroelastic/ferroelectric transformation at about 295 K follows the group–subgroup relation orthorhombic  $2'22' \longleftrightarrow$  monoclinic 121 (index  $[i] = 2$ ) with  $\beta \approx 90^\circ$ . The primed operations form the coset of the group–subgroup relation and thus the twin law. Owing to the small deviation of the angle  $\beta$  from  $90^\circ$ , the lattices of both twin partners nearly coincide. Note that this group–subgroup relation involves both an orthorhombic merohedral and a monoclinic merohedral point group, *viz* 222 and 2.

(2) Transformation twins orthorhombic  $2'/m'2/m2'/m' \longleftrightarrow$  monoclinic  $12/m1$  with  $\beta \approx 90^\circ$ . This is a case analogous to that of Rochelle salt, except that the point groups involved are the holohedries of the orthorhombic and of the monoclinic crystal system,  $mmm$  and  $2/m$  [example:  $\text{KH}_3(\text{SeO}_3)_2$ ; Shuvalov *et al.* (1967)].

<sup>6</sup> Some authors use the term *superlattice* instead of *sublattice* because of its larger unit cell, or the term *derivative lattice*; for the latter term see Chapter 13.2 of Volume A of this series (Billiet & Bertaut, 2005)

### 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

(3) Pseudo-hexagonal growth twins of an orthorhombic  $C$ -centred crystal with  $b/a \approx \sqrt{3}$  and twin reflection planes  $m'(110)$  and  $m'(\bar{1}10)$ . The lattices of the three domain states nearly coincide and form a 'pseudo-coincidence lattice' of lattice index  $[j] = 1$ , but of point-group index  $[i] = 3$ , with subgroup  $\mathcal{H} = 2/m2/m2/m$  and supergroup  $\mathcal{K}(6) = 6(2)/m2/m2/m$  (cf. Example 3.3.6.8). Here, in contrast to exact merohedry, in single-crystal X-ray diffraction patterns most reflection spots will be split into three. Note that the term 'index' appears twice, first as the subgroup index  $[i] = 3$  of the point groups and second as the lattice index  $[j] = 1$  of the twin lattice: further details are given in Section 3.3.11.5.2.

#### 3.3.9.2.3. Twinning with partial lattice coincidence (lattice index $[j] > 1$ )

For these twins with partial but *exact* coincidence Friedel has coined the terms 'twinning by reticular merohedry' or 'by lattice merohedry'. Here the term merohedry refers only to the sublattice, *i.e.* to Case (2) above. Typical examples with  $[j] = 3$  and  $[j] > 3$  were described in Section 3.3.8.3. In addition to the sublattice relations, it is reasonable to include the point-group relations as well. Four examples are presented:

(1) Twinning of rhombohedral crystals (lattice index  $[j] = 3$ , example  $\text{FeBO}_3$ ). The *eigensymmetry* point groups of the structure and of the  $R$  lattice (of the untwinned crystal) are both  $\mathcal{H} = \bar{3}2/m$ . The extension of the *eigensymmetry* by the (binary) twin operation  $2_z$ , as described in Example 3.3.6.6, leads to the composite symmetry  $\mathcal{K} = 6'/m(\bar{3})2/m2'/m'$ , *i.e.* the point-group index is  $[i] = 2$ . The sublattice index is  $[j] = 3$ , because of the elimination of the centring points of the original triple  $R$  lattice in forming the hexagonal  $P$  twin lattice; cf. Section 3.3.11.4.2.

(2) Reflection twinning across  $\{2130\}$  or  $\{1450\}$ , or twofold rotation twinning around  $\langle 540 \rangle$  or  $\langle 230 \rangle$  of a hexagonal crystal with a  $P$  lattice (lattice symmetry  $6/m2/m2/m$ ). The twin generates a hexagonal coincidence lattice of index  $[j] = 7$  ( $\Sigma 7$ ) with  $\mathbf{a}' = 3\mathbf{a} + 2\mathbf{b}$ ,  $\mathbf{b}' = -2\mathbf{a} + \mathbf{b}$ ,  $\mathbf{c}' = \mathbf{c}$ . The hexagonal axes  $\mathbf{a}'$  and  $\mathbf{b}'$  are rotated around  $[001]$  by an angle of  $40.9^\circ$  with respect to  $\mathbf{a}$  and  $\mathbf{b}$ . The intersection lattice point group of both twin partners is  $6/m$ . The extension of this group by the twin operation 'reflection across  $\{2130\}$ ' leads to the point group of the coincidence lattice  $6/m2'/m'2'/m'$  (referred to the coordinate axes  $\mathbf{a}'$ ,  $\mathbf{b}'$ ,  $\mathbf{c}'$ ). The primed operations define the coset (twin law). For hexagonal lattices rotated around  $[001]$ , the  $\Sigma 7$  coincidence lattice ( $[j] = 7$ ) is the smallest sublattice with lattice index  $[j] > 1$  (least-diluted hexagonal sublattice). No example of a hexagonal  $\Sigma 7$  twin seems to be known; for details see Section 3.3.11.4.2.

(3) Tetragonal growth twins with  $[j] = 5$  ( $\Sigma 5$  twins) in  $\text{SmS}_{1.9}$  (Tamazyan *et al.*, 2000b). This rare twin is illustrated in Fig. 3.3.8.1 and is described, together with the twins of the related phase  $\text{PrS}_2$ , in Example (3) of Section 3.3.9.2.4 below.

(4) Reflection twins across a general net plane ( $hkl$ ) of a cubic lattice. This example has been treated already in Section 3.3.9.1, Case (2).

#### 3.3.9.2.4. Twinning with partial lattice pseudo-coincidence (lattice index $[j] > 1$ )

This type can be derived from the category in Section 3.3.9.2.3 above by relaxation of the condition of exact lattice coincidence, resulting in two nearly, but not exactly, coinciding lattices (pseudo-coincidence, cf. Section 3.3.8.4). In this sense, the two Sections 3.3.9.2.3 and 3.3.9.2.4 are analogous to the two Sections 3.3.9.2.1 and 3.3.9.2.2.

The following four examples are characteristic of this group:

(1) ( $110$ ) reflection twins of a pseudo-hexagonal orthorhombic crystal with a  $P$  lattice: If the axial ratio  $b/a = \sqrt{3}$  were exact, the lattices of both twin partners would coincide exactly on a sublattice of index  $[j] = 2$  (due to the absence of the  $C$  centring);

cf. Koch (2004), Fig. 1.3.2.2. If  $b/a$  deviates slightly from  $\sqrt{3}$ , the exact coincidence lattice changes to a pseudo-coincidence lattice of lattice index  $[j] = 2$ . Examples are ammonium lithium sulfate,  $\text{NH}_4\text{LiSO}_4$  (Hildmann, 1980), many members of the  $\text{K}_2\text{SO}_4$ -type series (cf. Docherty *et al.*, 1988) and aragonite,  $\text{CaCO}_3$ ; for further details see Section 3.3.11.5.2.

(2) *Staurolite twinning*: This topic has been extensively treated as Example 3.3.6.13. The famous  $90^\circ$ - and  $60^\circ$ -twin 'crosses' are a complicated and widely discussed example for Friedel's notion of 'twinning by reticular merohedry' (Friedel, 1926, p. 461). It was followed up by an extensive analysis by Hurst *et al.* (1956). Both twin laws ( $90^\circ$  and  $60^\circ$  crosses) can be geometrically derived from a multiple pseudo-cubic cell  $\mathbf{a}'_c$ ,  $\mathbf{b}'_c$ ,  $\mathbf{c}'_c$  (so-called 'Mallard's pseudo-cube') which is derived from the structural monoclinic  $C$ -centred cell  $\mathbf{a}_m$ ,  $\mathbf{b}_m$ ,  $\mathbf{c}_m$  as follows, involving a rotation of  $\sim 45^\circ$  around  $[100]$ :

$$\mathbf{a}'_c = \mathbf{b}_m + 3\mathbf{c}_m, \quad \mathbf{b}'_c = -\mathbf{b}_m + 3\mathbf{c}_m, \quad \mathbf{c}'_c = 3\mathbf{a}_m.$$

Using Smith's (1968) lattice constants for the structural monoclinic cell with space group  $C2/m$  and  $a = 7.871$ ,  $b = 16.620$ ,  $c = 5.656$  Å,  $\beta = 90^\circ$  (within the limits of error),  $V_m = 740$  Å<sup>3</sup>, the pseudo-cube has the following lattice constants:

$$\begin{array}{lll} a'_c = 23.753 & b'_c = 23.753 & c'_c = 23.613 \text{ \AA} \\ \alpha_c = 90 & \beta_c = 90 & \gamma_c = 88.81^\circ \quad V'_c = 13323 \text{ \AA}^3. \end{array}$$

The volume ratio  $V'_c/V_m$  of the two cells is 18, *i.e.* the sublattice index is  $[j] = 18$ . If, however, the primitive monoclinic unit cell is used, the volume ratio doubles and the sublattice index used in the twin analysis increases to  $[j] = 36$ . The (metrical) *eigensymmetry* of the pseudo-cube is orthorhombic (due to  $\beta_c = 90^\circ$ ),  $(2/m)_{[001]}(2/m)_{[110]}(2/m)_{[\bar{1}\bar{1}0]}$ , referred to  $\mathbf{a}'_c$ ,  $\mathbf{b}'_c$ ,  $\mathbf{c}'_c$ .

Note, however, that this pseudo-cube in reality is  $C$ -centred because the  $C$ -centring vector  $1/2(\mathbf{a}'_c + \mathbf{b}'_c) = 3\mathbf{c}_m$  is a lattice vector of the monoclinic lattice. This  $C$ -centring has not been considered by Friedel, Hurst and Donnay, who have based their analysis on the primitive pseudo-cube.

According to Friedel, the 'symmetry elements' of the pseudo-cube are potential twin elements of staurolite, except for  $(2/m)_{[\bar{1}\bar{1}0]}$ , which is the monoclinic symmetry direction of the structure. In Table 3.3.9.1, the twin operations of the  $90^\circ$  and  $60^\circ$  twins are compared with the 'symmetry operations' of the pseudo-cube with respect to obliquities  $\omega$  and lattice indices  $[j]$ , referred to both sets of axes, pseudo-cubic  $\mathbf{a}'_c$ ,  $\mathbf{b}'_c$ ,  $\mathbf{c}'_c$  and monoclinic (but metrically orthorhombic)  $\mathbf{a}_m$ ,  $\mathbf{b}_m$ ,  $\mathbf{c}_m$ . The calculations were again performed with the program *OBLIQUE* by Le Page (1999, 2002). In order to keep agreement with the interpretation of Friedel and Hurst *et al.*, the pseudo-cube is treated as primitive, with  $[j] = 36$ .

The following interpretations can be given (cf. Fig. 13 in Hurst *et al.*, 1956):

(a)  $90^\circ$  cross (Table 3.3.9.1a, Fig. 3.3.6.15a):

(i) The pseudo-tetragonal  $90^\circ$  cross can be explained and visualized very well with eight twin operations, a fourfold twin axis along  $[100]_m = [001]_c$  with operations  $4^1$ ,  $4^3$ ,  $\bar{4}^1$ ,  $\bar{4}^3$  and two pairs of 'diagonal' twin operations  $2$  and  $m$ . They form the coset of the (metrically) 'orthorhombic' ( $\beta = 90^\circ$ ) *eigensymmetry*  $\mathcal{H} = mmm$  which results in the composite symmetry  $\mathcal{K} = 4'(2)/m2/m2'/m'$ .

(ii) The obliquities for all twin operations are at most  $1.2^\circ$ , the lattice index is  $[j]_m = 1$  for the twin axis, but for the 'diagonal' twin elements it is  $[j]_m = 6$ , which is at the limit of the permissible range. Because of these facts, Friedel prefers to consider the  $90^\circ$  cross as a  $90^\circ$  rotation twin around  $[100]_m$  rather than as a (diagonal) reflection twin across  $(031)_m$  or  $(0\bar{3}1)_m$ .

(iii) Note that for the interpretation of the  $90^\circ$  cross the complete pseudo-cube with lattice index  $[j] = 36$  is not required.

### 3.3. TWINNING OF CRYSTALS

Because  $\mathbf{c}'_c = 3\mathbf{a}_m$ , a pseudo-tetragonal unit cell with axes  $\mathbf{a}'_c, \mathbf{b}'_c, (1/3)\mathbf{c}'_c$  and  $[j] = 12$  is sufficient.

(b) 60° cross (Table 3.3.9.1b, Fig. 3.3.6.15b):

(iv) The widespread 60° cross is much more difficult to interpret and visualize. The four threefold twin axes around  $\langle 111 \rangle$  of the pseudo-cube split into two pairs, both with very small obliquities  $< 1^\circ$ . One pair,  $[102]_m$  and  $[\bar{1}02]_m$ , has a favourable index  $[j]_m = 3$ ; however, the other one,  $[320]_m$  and  $[3\bar{2}0]_m$  is with  $[j]_m = 9$  unacceptably high. According to Friedel's theory, this makes  $[102]_m$  the best choice as threefold twin axis.

(v) There is a further  $\pm 90^\circ$  twin rotation around  $[100]_c$  or  $[013]_m$  with small obliquity,  $\omega = 1.2^\circ$ , but very high lattice index,  $[j]_m = 6$ . Note that this is the same axis that has been used already for the 90° twin, but with a 180° rotation.

(vi) The greatest deviation from the 'permissibility' criterion is exhibited by the twin axes  $2[101]_c = 2[313]_m$  and  $2[011]_c = 2[3\bar{1}3]_m$  and the twin planes, pseudo-normal to them,  $(231)_m$  and  $(2\bar{3}1)_m$ . The obliquity  $\omega = 0.9^\circ$  is very good but the twin index is  $[j] = 12$ , a value far outside Friedel's 'limite prohibitive'. These operations, however, are the 'standard' twin operations that are always quoted for the 60° twins. Following Friedel (1926, p. 462), the best definition of the 60° twin are the  $\pm 120^\circ$  rotations around  $[102]_m$  with  $\omega = 0.87^\circ$  and  $[j]_m = 3$ .

(vii) If the (true) C-centring of the pseudo-cube is taken into account, however, no  $\langle 111 \rangle$  pseudo-threefold axes remain; hence, the 60° cross cannot be explained by the lattice construction of the pseudo-cube.

*Nespolo and Ferraris' description of the staurolite twins.* Nespolo & Ferraris (2005, 2006, 2007a,b) have formulated extensions of Mallard's and Friedel's lattice theory of twinning. They introduce 'hybrid twinning' (Nespolo & Ferraris, 2005, 2006), which involves more than one sublattice contributing to the 'overall lattice restoration', a new calculation of the twin index for 'manifold twins' ('multiple twins' in the present chapter, cf. Section 3.3.2.3.2) and a 'twin misfit  $\delta$ ' (Nespolo & Ferraris, 2007b), defined as 'the distance between the first nodes along the shortest direction in the plane quasi-perpendicular to the twin axis that are quasi-restored by the twin operation'.

Based on these considerations, the twin lattices of staurolite have been reconsidered (Nespolo & Ferraris, 2007a,b), with the following results in comparison to the discussion above by the present authors:

(i) For the 'Greek cross twins' (90° cross), the two treatments agree and result in the twin index  $[j] = 6$ , just at the limit of Friedel's rule for the occurrence of twinning.

(ii) The much more frequent 'St Andrews cross twins' (60° cross) have a twin index 12, far too high according to Friedel's standard. This discrepancy is eliminated by Nespolo & Ferraris (2007a) by considering this twin as a hybrid twin with two concurring monoclinic sublattices, generated by twin axis/plane  $[313]/(231)$  with index 12 (obliquity  $0.90^\circ$ ) and  $[313]/(352)$  with index 10 (obliquity  $6.21^\circ$ ). Since two of the nodes of the  $[313]/(231)$  sublattice are quasi-coincident with nodes of the sublattice  $[313]/(352)$ , the index 12 is reduced by a factor 2 to an effective index 6, comparable to index 6 of the 90° twin and, thus, just acceptable by Friedel's criterion, but with one large obliquity of  $6.21^\circ$ .

(iii) The last paper in the series (Nespolo & Ferraris, 2007b) is a critical discussion of the twin-lattice treatment of previous authors, including the present ones. Its essential statement is that the Friedel criterion is applicable *only* to binary twin operations, *not* to 'manifold twins' ('multiple twins', see above), for which a new twin index is defined. This index is now the same for all operations in the coset of the manifold twin. For the Greek cross (90° twin), Nespolo & Ferraris arrive at the same result (index 6) as the present authors. For the 'St Andrews cross' (60° twin) there is a significant difference in the two approaches: the present authors believe that the 60° cross cannot be explained by the lattice construction of 'Mallard's pseudo-cube' because the C-centred cubic twin lattice, which is actually tetragonal  $P$  with  $c/a = 1:\sqrt{2}/2$ , has no pseudo-threefold axis along any  $\langle 111 \rangle$  direction which could act as a threefold twin rotation axis. Nespolo & Ferraris, on the other hand, disregard the C-centring of the Mallard's pseudo-cube and explain the 60° twin by the threefold axes of the cubic  $P$  cell (see their Fig. 1 and the trichromatic twin point group given on their page 285), as was done by Mallard (1879), Friedel (1926) and Donnay & Donnay (1983).

(3) *Growth twins of monoclinic PrS<sub>2</sub> and of tetragonal SmS<sub>1.9</sub>.* These two rather complicated examples belong to the structural family of  $MeX_2$  dichalcogenides which is rich in structural relationships and different kinds of twins. The 'basic structure' and 'aristotype' of this family is the tetragonal  $ZrSSi$  structure with axes  $a_b = b_b \approx 3.8$ ,  $c_b \approx 7.9$  Å,  $V_b \approx 114$  Å<sup>3</sup>, space group  $P4/nmm$  ( $b$  stands for basic). The

Table 3.3.9.1. *Staurolite, 60° and 90° twins*

Comparison of the twin operations with the 'symmetry operations' of the primitive pseudo-cube with respect to obliquity  $\omega$  and lattice index  $[j]$ , referred both to the pseudo-cubic axes,  $\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$ , and the monoclinic (metrically orthorhombic) axes,  $\mathbf{a}_m, \mathbf{b}_m, \mathbf{c}_m$ . The calculations were performed with the program *OBLIQUE* by Le Page (1999, 2002).

(a) 90° cross (eight twin operations).

Twin operations referred to		Obliquity $\omega$ [°]	Lattice index $[j]$ referred to		Remarks
$\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$	$\mathbf{a}_m, \mathbf{b}_m, \mathbf{c}_m$		$\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$	$\mathbf{a}_m, \mathbf{b}_m, \mathbf{c}_m$	
$4[001]_c$	$4[100]_m$	0	1	1	Four collinear twin operations $4^1, 4^3, \bar{4}^1, \bar{4}^3$
$2[100]_c$	$2[013]_m$	1.19	1	6	Four 'diagonal' (with respect to the monoclinic unit cell) twin operations intersecting in $[001]_c = [100]_m$
$m(100)_c$	$m(031)_m$	1.19	1	6	
$2[010]_c$	$2[0\bar{1}3]_m$	1.19	1	6	
$m(010)_c$	$m(0\bar{3}1)_m$	1.19	1	6	

(b) 60° cross.

Twin operations referred to		Obliquity $\omega$ [°]	Lattice index $[j]$ referred to		Equivalent directions
$\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$	$\mathbf{a}_m, \mathbf{b}_m, \mathbf{c}_m$		$\mathbf{a}'_c, \mathbf{b}'_c, \mathbf{c}'_c$	$\mathbf{a}_m, \mathbf{b}_m, \mathbf{c}_m$	
$3[111]_c$ ( $\pm 120^\circ$ )	$3[102]_m$	0.87	3	3	$[11\bar{1}]_c = [\bar{1}02]_m$
$3[\bar{1}\bar{1}1]_c$ ( $\pm 120^\circ$ )	$3[320]_m$	0.25	3	9	$[\bar{1}\bar{1}1]_c = [3\bar{2}0]_m$
$4[100]_c$ ( $\pm 90^\circ$ )	$4[013]_m$	1.19	1	6	$[010]_c = [0\bar{1}3]_m$
$m(100)_c$	$m(031)_m$	1.19	1	6	
$2[101]_c$	$2[313]_m$	0.90	1	12	$[011]_c = [3\bar{1}3]_m$
$m(101)_c$	$m(231)_m$	0.90	1	12	$[101]_c = [313]_m$ $[011]_c = [313]_m$

### 3. SYMMETRY ASPECTS OF PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

crystal chemistry of this structural family is discussed by Böttcher *et al.* (2000).

#### (a) $PrS_2$ (Tamazyán *et al.*, 2000a)

$PrS_2$  is a monoclinic member of this series with space group  $P2_1/b11$  (unique axis  $a_3^!$ ) and axes  $a \approx 4.1$ ,  $b \approx 8.1$ ,  $c \approx 8.1$  Å,  $\alpha \approx 90.08^\circ$ ,  $V \approx 269$  Å<sup>3</sup>. The structure is strongly pseudo-tetragonal along [001] (with cell  $a$ ,  $b/2$ ,  $c$ ) and is a ‘derivative structure’ of ZrSSi. Hence pseudo-merohedral twinning that makes use of this structural tetragonal pseudosymmetry would be expected, with twin elements  $4[001]$  or  $m(210)$  or  $2[120]$  *etc.* and  $[j] = 2$  because  $b \approx 2a$ , but, surprisingly, this twinning has not been observed so far. It may occur in other  $PrS_2$  samples or in other isostructural crystals of this series.

Instead, the monoclinic crystal uses another structural pseudosymmetry, the approximate *orthorhombic* symmetry along [100] with  $\alpha \approx 90^\circ$ , to twin on  $2_y$ ,  $2_z$ ,  $m_x$ , or  $m_z$  (coset of  $2_x/m_x$ ) with composite symmetry  $\mathcal{K} = 2/m'2'/m'2'/m'$ ,  $[j] = 1$  and  $[i] = 2$  (*cf.* Fig. 4 of the paper).

The monoclinic  $PrS_2$  cell has a third kind of pseudosymmetry that is not structural, only metrical. The cell is pseudo-tetragonal along [100] due to  $b \approx c$  and  $\alpha \approx 90^\circ$ . This pure lattice pseudosymmetry, not surprisingly, is not used for twinning, *e.g.* via  $4[100]$  or  $m(011)$  or  $m(0\bar{1}1)$  or  $2[011]$  or  $2[0\bar{1}1]$ .

#### (b) $SmS_{1.9}$ (Tamazyán *et al.*, 2000b)

This structure is (strictly) tetragonal with axes  $a = b \approx 8.8$ ,  $c \approx 15.9$  Å,  $V \approx 1238$  Å<sup>3</sup> and space group  $P4_2/n$ . It is a tenfold superstructure of ZrSSi with the following basis-vector relations:

$$\mathbf{a} = 2\mathbf{a}_b + \mathbf{b}_b, \quad \mathbf{b} = -\mathbf{a}_b + 2\mathbf{b}_b, \quad \mathbf{c} = 2\mathbf{c}_b,$$

leading to lattice constants  $a \approx \sqrt{5}a_b$ ,  $b \approx \sqrt{5}b_b$ ,  $c \approx 2c_b$ . This well ordered tetragonal supercell now twins on  $m(210)$  or  $2[210]$  or  $m(130)$  or  $2[130]$  (which is equivalent to a rotation around [001] of  $36.87^\circ$ ) to form a  $\Sigma 5$  twin by ‘reticular merohedry’ ( $[j] = 5$ ) with lattice constants  $a' = a\sqrt{5} = 19.72$ ,  $b' = b\sqrt{5} = 19.72$ ,  $c' = c = 15.93$  Å,  $V = 6192$  Å<sup>3</sup>. This is illustrated in Fig. 3.3.8.1.

$SmS_{1.9}$  represents the first thoroughly investigated and documented tetragonal  $[j] = 5$  ( $\Sigma 5$ ) twin known to us. The sublattice of this twin is the tetragonal coincidence lattice with smallest lattice index  $[j] > 1$ , *i.e.* the ‘least-diluted’ systematic tetragonal sublattice; for further details see Section 3.3.11.4.2.

(4) *Growth twins of micas*: A rich selection of different twin types, both merohedral and pseudo-merohedral, with  $[j] = 1$  and 3, is provided by the mineral family of micas, which includes several polytypes. A review of these complicated and interesting twinning phenomena is presented by Nespolo *et al.* (1997). Detailed theoretical derivations of mica twins and allotwins, both in direct and reciprocal space, are published by Nespolo *et al.* (2000).

In conclusion, it is pointed out that the above four categories of twins, described in Sections 3.3.9.2.1 to 3.3.9.2.4, refer only to cases with exact or approximate *three-dimensional* lattice coincidence (*triperiodic twins*). Twins with only two- or one-dimensional lattice coincidence (*diperiodic* or *monoperiodic* twins) [*e.g.* the (100) reflection twins of gypsum and the (101) rutile twins] belong to other categories, *cf.* Section 3.3.8.2. The examples above have shown that for triperiodic twins *structural* pseudosymmetries are an essential feature, whereas purely *metrical (lattice)* pseudosymmetries are not a sufficient tool in explaining and predicting twinning, as is evidenced in particular by the case of staurolite, discussed above in detail.

#### 3.3.9.3. Pseudo-merohedry and ferroelasticity

The large group of pseudo-merohedral twins (irrespective of their lattice index) contains a very important subset which is characterized by the physical property *ferroelasticity*. Ferroelastic twins result from a real or virtual phase transition involving a

change of the crystal family (crystal system). These transitions are displacive, *i.e.* they are accompanied by only small structural distortions and small changes of lattice parameters. The structural symmetries lost in the phase transition are preserved as pseudosymmetries and are thus candidates for twin elements. This leads to a pseudo-coincidence of the lattices of the twin partners and thus to pseudo-merohedral twinning. Because of the small structural changes involved in the transformation, domains usually switch under mechanical stress, *i.e.* they are ferroelastic. A typical example for switchable ferroelastic domains is Rochelle salt, the first thoroughly investigated ferroelastic transformation twin, discussed in Section 3.3.9.2.2, Example (1). This topic is extensively treated in Chapter 3.4 on domain structures.

### 3.3.10. Twin boundaries

#### 3.3.10.1. Contact relations in twinning

So far, twinning has been discussed only in terms of symmetry and orientation relations of the (bulk) twin components. In this chapter, the very important aspect of *contact relations* is discussed. This topic concerns the orientation and the structure of the *twin boundary*, which is also called twin interface, composition plane, contact plane, domain boundary or domain wall. It is the twin boundary and its structure and energy which determine the occurrence or non-occurrence of twinning. In principle, for each crystal species an infinite number of orientation relations obey the requirements for twinning, as set out in Section 3.3.2, because any rational lattice plane ( $hkl$ ), as well as any rational lattice row  $[uvw]$ , common to both partners would lead to a legitimate reflection or rotation twin. Nevertheless, only a relatively small number of crystal species exhibit twinning at all, and, if so, with only a few twin laws. This wide discrepancy between theory and reality shows that a permissible crystallographic orientation relation (twin law) is a necessary, but not at all a sufficient, condition for twinning. In other words, the *contact relations* play the decisive role: a permissible orientation relation can only lead to actual twinning if a twin interface of good structural fit and low energy is available.

In principle, a twin boundary is a special kind of grain boundary connecting two ‘homophase’ component crystals which exhibit a crystallographic orientation relation, as defined in Section 3.3.2. For a given orientation relation of the twin partners, crystallographic or general, the interface energy depends on the orientation of their boundary. It is intuitively clear that crystallographic orientation relations lead to energetically more favourable boundaries than noncrystallographic ones. As a rule, twin boundaries are planar (at least in segments), but for certain types of twins curved and irregular interfaces have been observed. This is discussed later in this section.

In order to determine theoretically for a given twin law the optimal interface, the interface energy has to be calculated or at least estimated for various boundary orientations. This problem has not been solved for the general case so far. The special situation of reflection twins with coinciding twin mirror and composition planes has recently been treated by Fleming *et al.* (1997). These authors calculated the interface energies for three possible reflection twin laws in each of aragonite, gibbsite, corundum, rutile and sodium oxalate, and they compared the results with the observed twinning. In all cases, the twin law with lowest boundary energy corresponds to the twin law actually observed. Another calculation of the twin interface energy has been performed by Lieberman *et al.* (1998) for the (102) reflection twins of monoclinic saccharin crystals. In this study, the (102) boundary energy was calculated for different shifts of the two twin components with respect to each other. It was shown that a minimum of the boundary energy is achieved for a particular ‘twin displacement vector’ (*cf.* Section 3.3.10.4.1).